The electro- and photoluminescence spectra
of oxide films formed during anodic oxidation of zinc

Roman Dragon

Physics Laboratory, Institute of Mathematics and Physics, Higher School of Engineering, Opole, Poland.

Distribution of intensity in stationary anodic electroluminescence spectrum of zinc electrodes has been determined and compared with the photoluminescence spectrum of dried anodic zinc oxide films formed in the same electrolyte. It has been found that the anodic electroluminescence spectrum has its maximum in the green part (520 nm), whereas the photoluminescence spectrum of dried oxide films in the yellow part (580 nm). A hypothesis explaining the appearance of both spectra in different parts of the visible spectral region has been suggested.

1. Introduction

Anodic oxidation of zinc electrodes in some electrolytes is accompanied by luminescence. The luminescence effect of zinc anodes was already mentioned by Braun [1], Lavaux [2], and Dufford [3]. In newer times Krieg and Lange [4] observed again the luminescence of zinc anode during anodic polishing of zinc in concentrated aqueous solutions of NaOH. They regarded the luminescence as being the result of electroluminescence of a thin zinc oxide film which was formed on the anode. In the above mentioned papers no photometric or spectral examinations of the luminescence have been conducted.

The author of the present paper examined the luminescence of zinc anodes occurring during electrolytic oxidation [5] as well as luminescence and photoelectric properties of dried anodic zinc oxide films [6]. However, in these papers the spectral distribution of the luminescence has not been performed. The aim of the present paper is to present and compare the anodic electroluminescence spectrum of zinc electrodes with the photoluminescence spectrum of dried anodic zinc oxide films.

2. Experimental conditions

Zinc (purity of 99.98%) in the form of plates was used for experiments. The spectral analysis has shown that traces of Pb, Cu, Cd, Ag and Cr admixtures are present in the investigated material. Before the process of electrolytic oxi-

dation, zinc plates were chemically polished in order to remove any surface impurities. The electrolytic oxidation of zinc plates was conducted in the mixture of $Na_2CO_3/NaOH$ made of aqueous solutions: 0.5 m Na_2CO_3 and 1 n NaOH taken in voluminal ratio 7:1. During the process of electrolytic oxidation zinc plates were used as anodes, whereas platinum plate served as the cathode. The zinc anodes emitted light during the electrolytic oxidation.

Figure 1 presents the scheme of the measuring set-up used to study the spectral distribution of intensity of the observed electroluminescence of zinc
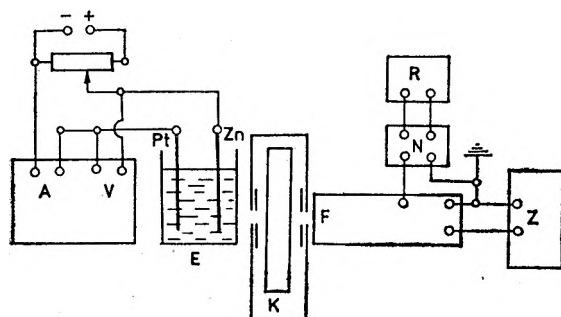
Fig. 1. Scheme of spectrum measuring instruments: F – photomultiplier, K – interference Schott wedge, Z – feeder, N – amplifier, R – recorder, A, V – double recorder, E – electrolytic cell

anodes. The basic elements of the apparatus was an interference wedge Veril S-200 made by Schott Co. The wedge was placed in a well-fitted casing with two slots 2 mm wide and 15 mm high being opposite to each other. The wedge was shifted automatically towards the slots by a synchronous motor. The speed of shift was chosen in such a way that the spectrum interval ranging from 400 nm to 600 nm could be registered in the course of 1.5 min. Half-width of radiation band passing through the wedge was 12 nm. The light of zinc anodes, after passing through the interference wedge, fell on the photocathode of photomultiplier type FEU-27. Photocurrent was amplified by *d.c.* amplifier and recorded by the recorder type Norma.

The same photometric apparatus was used to measure the photoluminescence spectra of anodic zinc oxide films. In front of the interference wedge there was a proper adjustage inside of which an anodized zinc plate was placed.
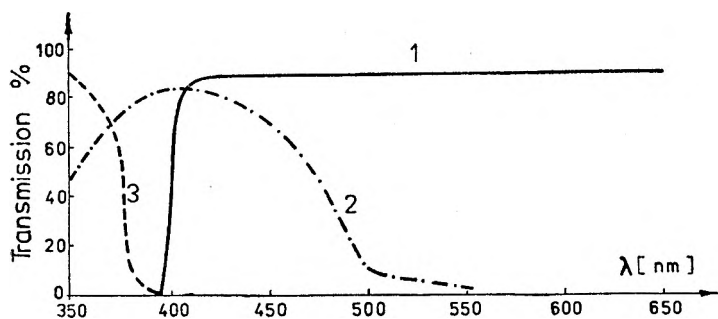
Fig. 2. Filter transmission curves: 1 – aqueous solution of sodium nitrite, 2 – filter BG12, 3 – filter UG11

The sample was excited with UV light emitted by a quartz-lamp type Q400 and passing through the filters BG12 and UG11. The system consisting of such a combination of filters permits practically to isolate the 365 nm line from the mercury spectrum. In front of the input slot of the interference wegde there was also a water filter – aqueous solution of sodium nitrite in a quartz vessel. The solution of sodium nitrite absorbed UV light reflected partially from the sample and almost completely transmitted visible light which was emitted by the sample. The light transmission curves of the filters used are shown in Fig. 2.

3. Results of experiments

The obtained results are presented in Figure 3. Curve 1 presents the distribution of intensity in a stationary anodic electroluminescence spectrum of zinc plate after 10 minutes from the beginning of oxidation of the plate in the aqueous
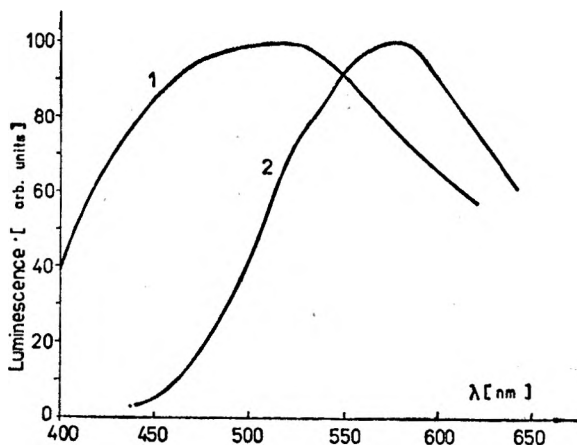

Fig. 3. Emission spectra of anodic zinc oxide films: 1 – electroluminescence, 2 – photoluminescence

mixture of $Na_2CO_3/NAOH$. Direct current voltage on the electrolytic cell was 55 V and anodic current density was 10 mA/cm². It can be seen that the emission band of the anodic electroluminincesence of zinc electrode is very wide and has its maximum at about 520 nm. From the curve of spectral distribution it can be concluded that the electroluminescence spectrum is extended to the ultraviolet region.

    The occurrence of the ultraviolet component in the anodic emission was found experimentally while examining the anodic luminescence of zinc plate through filters UG11 (2 mm thick) and the aqueous solution of sodium nitrite placed in a quartz vessel (5 mm thick). During these experiments a photomultiplier type FEU-19M was used. Its spectral sensitivity ranges from 300 nm to about 650 nm. The change of the photomultiplier was caused by the fact that filter UG11 was partially transparent for the light of the wavelength greater than 650 nm.

No luminescence has been recorded when both filters were placed between the photomultiplier and the anodic polarized zinc electrode. However, distinct anodic emission could be recorded when each filter was used separately. From the curves of spectral sensitivity of the photomultiplier type FEU-19 and from the light transmission of both filters (Fig. 2) it appears that the light recorded by the photomultiplier after passing through filter UG11 lies in the ultraviolet region, whereas the light which was let through the aqueous solution of sodium nitrite lies in the visible region. In that case it can be assumed that during the anodic emission there occurs ultraviolet radiation aparat from visible radiation. The distribution of ultraviolet component spectrum was not examined due to the lack of a suitable set of filters.

Curve 2 in Figure 3 presents the photoluminescence spectrum of dried anodic oxide film which was previously formed in the aqueous mixture of $Na_2CO_3/NaOH$ at a voltage of 50 V in the course of half an hour. From the comparison of both curves it can be seen that the spectra are different. The photoluminescence spectrum of anodic oxide films shows a wide emission band in the yellow and red regions with the maximum of its intensity corresponding to the wavelength of about 580 nm, whereas the electroluminescence spectrum has its maximum in the green region.

4. Discussion

The anodic emission of zinc electrodes comes probably from the thin compact oxide films which is directly close to metal. Since the voltage applied to the electrolytic cell drops almost totally on the film, the intensity of electric field in this film is high. Pores that appear in the oxide film as a consequence of the dissolving action of the electrolyte are soon filled with the electrolyte. Thus, on the basis of the compact oxide film greater porous film is produced.

From the theory of growth of anodic oxide films on valve metals [7–8] it follows that the current flowing through oxide film during its growth is mostly ionic and only its small part has electronic nature. The greater part of electron current flows probably through the compact oxide film which separates the porous part from metal. In the other porous part of oxide film the charge is carried mainly by ions present in the electrolyte filling the pores.

In order to explain qualitatively the anodic electroluminescence of zinc electrodes it has been assumed that like (see [9–11]) to the case of the anodic electroluminescence of aluminium electrodes the anodic emission is caused by the electron component of the current flowing through the oxide film, and that the excitation of luminescence centres is caused by the non-elastic collision with fast electrons. The collision theory of the excitation of centres in electro-luminescent phosphors has been first suggested by Destriau, thereupon it was elaborated thoroughly by Curie and quite independently by Piper and Williams [12, 13]. The excitation mechanism of luminescence centres in phosphor, result-

ing from the collision with the electrons accelerated through an electric field, requires the existence of regions characterized by high field intensity (10^5–10^6 V/cm) and a number of primary electrons present in the region. The evaluation of physical conditions existing in the anodic oxide films formed on zinc leads to the conclusion that these conditions may be satisfied.

Because of the asymmetry of the electric conductivity shown by the system Zn-ZnO-electrolyte [5, 14] it may be assumed that a potential barrier is formed in the oxide film, being in contact with the electrolyte during the anodic bias of zinc plate. The energy bands of oxide are curved, as shown in Fig. 4.
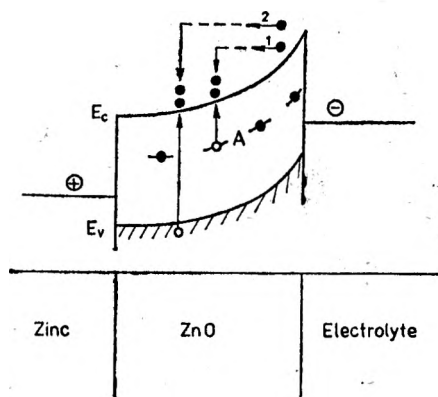

Fig. 4. Energy model of contact of anodic oxide film – electrolyte with applied blocking voltage: E_c and E_v denote bottom of conduction band and ceiling of valency band, respectively; A – activator levels, ($\bullet$ – electron, o – hole)

Due to the adsorption of negative oxygen ions on the surface of anodic zinc oxide film and to their partial diffusion to the surface oxide zone, the surface of films shows the resultant negative charge. The formation of compensating space charge in the bulk of the oxide causes the appearance of potential barrier.

The mean value of electric field existing in the oxide film may be evaluated as the ratio of the voltage applied to the electrolytic cell to the thickness of oxide film. For this purpose the thickness of oxide films was estimated for various forming voltages. Figure 5 presents the results of measurements of the thickness of oxide films formed on zinc in the aqueous mixture of Na_2CO_3/NaOH in the
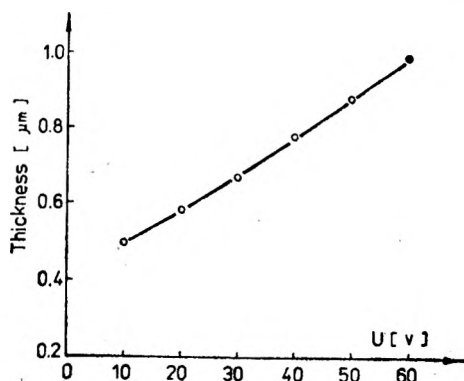

Fig. 5. Thickness of anodic zinc oxide films versus the forming voltage

course of 20 minutes, at various forming voltages. The thickness of films was determined by the gravimetric method given by FISCHER and BUDILOFF [15]; moreover a simplified assumption was made that the density of anodic ZnO was about 5 g/cm^3. The thickness of oxide films determined in this way must be treated as approximate. The films being porous, the results presented in Fig. 5 give the total thickness of films, i.e., the sum of thickness of cohesive and porous parts. Obviously, the thickness of cohesive parts of an oxide film is smaller than that of the whole film. From this figure it may be estimated that at a forming voltage of 55 V the mean field intensity in the film is about $6 \cdot 10^5$ V/cm. In reality, the field intensity in the cohesive film is probably much greater. The order of magnitude of the electric field is thus sufficient to give the electrons, present in the region of this field, a proper kinetic energy necessary for the ionization of luminescence centres.

Primary electrons, responsible for the anodic emission, come from anions which are discharged partially at the boundary of electrolyte-anodic oxide film. The electrons enter the region of the strong electric field where they receive a sufficient kinetic energy and then they ionize the luminescence centres or create electron-hole pairs in the oxide. Two electrons which enter the oxide conduction band and undergo acceleration in the region of a potential barrier are presented schematically in Fig. 4. For instance, electron 1, after receiving a sufficient energy can ionize the center, whereas the electron 2 can transfer an electron from the valence band of oxide to the conduction band, thus forming a pair: electron-hole. The visible or ultraviolet luminescence accompanies the recombination of small-energy electrons occupying lower levels in the conduction band with the ionized luminescence centres or holes.

The proposed mechanism of the anodic electroluminescence of zinc electrodes would qualitatively explain the presence of visible and ultraviolet radiations in the anodic electroluminescence spectrum. The visible radiation arises from the recombination of conduction electrons with luminescence centres, whereas the ultraviolet radiation appears as a result of a direct recombination of electron-hole pairs. Although for zinc oxide the probability of radiative transition of an electron from the conduction band to the valence band should not be high, because of considerable value of the width of forbidden gap (3.2 V), nevertheless an ultraviolet component occurs also in spectrum when monocrystals of zinc oxide are excited by cathode rays [16]. Therefore, analogous transition can be expected in the anodic oxide films, excited by the electric field. The hypothesis may be supported by the fact that when the anodic oxide film is excited by a sinusoidal-alternating voltage, there occur brightness waves both in the visible and ultraviolet regions.

As it has been mentioned above, the emission bands of anodic zinc oxide films in the electro- and photoluminescence are different. The green band occurs, first of all, in the electroluminescence spectrum of anodic oxide films, whereas the yellow band appears in the photoluminescence spectrum. This fact may be explained in the following way: in the oxide films formed in the aqueous

mixture of $Na_2CO_3/NaOH$ there are two different kinds of luminescence centres, namely – *green* and *yelow* ones. Based on the literature data referring to zinc oxide obtained by other method it can be concluded that the green luminescence centres are connected with excess zinc atoms [17–19], and the yellow ones with excess oxygen atoms [17, 18, 20–23].

The differences between the observed photo- and electroluminescence spectra may be explained by the complex structure of these films. From the physicochemical experiments conduced by HUBER [24, 25] it follows that anodic zinc oxide films are heterogeneous and composed of a cohesive inner part being directly close to zinc and a porous outer part. Defects, playing a role of the green luminescence centres (excess zinc atoms) are probably concentrated in the thin cohesive zinc oxide film. During the anodic bias of zinc oxide film the green luminescence centres are excited in the result of non-elastic collisions with high energy electrons. Defects, being yellow luminescence centres (excess oxygen atoms), are concentrated in the porous otuer part of oxygen-rich zinc oxide film. During the formation of film in the electrolyte oxygen is adsorbed and probably partly built in the outer part of zinc oxide film. The pores existing in the film favour the process. During the anodic bias of zinc oxide film being in contact with the electrolyte, the prevailing part of electron component of anodic current flows through the cohesive film, thus, mainly the green luminescence centres undergo excitation. However, during the UV-radiation of film, the yellow luminescence centres are mainly excited probably due to the fact that the intensity of ultraviolet light decreases towards the inside of zinc oxide films.

References

[1] BRAUN F., Ann. Physik u. Chemie **65** (1898), 361.
[2] LAVAUX J., Compt. Rend. Acad. Sci. (Paris) **169** (1919), 180.
[3] DUFFORD R. T., J. Opt. Soc. Am. **18** (1929), 17.
[4] KRIEG M., LANGE E., Naturwiss. **39** (1952), 208.
[5] DRAGON R., Zeszyty Naukowe WSP w Opolu, Fizyka **9** (1964), 45 (in Polish).
[6] DRAGON R., ibidem, **4** (1964), 43; 5 (1966), 9; 9 (1969), 7.
[7] YOUNG L., *Anodic oxide films*, Academic Press, London, New York 1961.
[8] SAKGEIM L. N., *Elektroliticheskie kondensatory*, Izd. Gos. Energ., Moskva, Leningrad 1963.
[9] ANDERSON S., J. Appl. Phys. **14** (1943), 601.
[10] VAN GEEL W. Ch., PISTORIUS C. A., BOUMA B. C., Philips Res. Rep. **12** (1957), 465.
[11] RUZIEWICZ Z., Bull. Acad Polon. Sci., Ser. Sci. Chim. **8** (1960), 667.
[12] CURIE D., *Luminescencja fosforów krystalicznych*, PWN, Warszawa 1965 (in Polish).
[13] WRZESIŃSKA A. A., *Fotoluminatory i elektroluminatory krystaliczne*, PWN, Wrocław 1974 (in Polish).
[14] HUBER K., J. Electrochem. Soc. **100** (1953), 376.
[15] FISCHER H., BUDILOFF N., Z. Metallkunde 4 (1940), 100.
[16] ANDRESS B., Z. Phys. **170** (1962), 1.
[17] HEILAND G., MOLLWO E., STÖCKMANN F., Solid State Physics, Vol. 8, Academic Press, New York 1959.
[18] KROGER F. A., VINK H. J., J. Chem. Phys. **22** (1954), 250.

[19] Mollwo E., Z. Phys. **162** (1961), 557.
[20] Zelikin Y. M., Izv. Akad. Nauk SSSR, Ser. Fiz. **25** (1961), 461.
[21] Zelikin Y. M., Zhukovsky, Opt. i Spektr. **11** (1961), 397.
[22] Zelikin Y. M., Uspenskaya E. M., Opt. i Spektr. **18** (1965), 880.
[23] Bundel A. A. et al., Izv. Akad. Nauk SSSR, Ser. Fiz. **30** (1966), 637.
[24] Huber K., Helv. Chim. Acta **26** (1943), 1037, ibidem **26** (1943), 1253.
[25] Huber K., Z. Elektrochem. **55** (1951), 165.

Спектры излучения анодных слоев окиси цинка в электро- и фотолюминесценции

В статье показана спектральная кривая стационарной анодной электролюминесценции цинкового электрода и спектральная кривая фотолюминесценции сухих анодных слоев окиси цинка, образованных в том же самом электролите. Установлено, что спектр в видимой области анодной электролюминесценции имеет максимум в зеленой части (520 нм), а спектр фотолюминесценции сухих оксидных слоев цинка в желтой части (580 нм). Предложена гипотеза, объясняющая разный вид обоих спектров.